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14. ABSTRACT
The aim of the project was to develop strong permanent magnets using nanoparticles and their composites. For this an understanding of the magnetic properties of nanoparticles was also needed. Assemblies of nanoparticles can be used to develop novel exchange coupled strong magnets without using rare earths as well as for high density magnetic recording media. Some of these nanoparticles (such as Fe-Pt) can also be very interesting for catalysis. Fe-Pt is one of the most promising materials due to its large magnetic anisotropy. *Ab initio* calculations on Fe-Pt nanoalloys (clusters and nanoparticles) were performed to understand the atomic and electronic structure, and the magnetic behavior. The findings revealed a tendency for Pt segregation on the surface and a preference for maximizing Fe-Pt bonds. The formation energy of the nanoalloys is the highest around 50:50 composition as also in bulk Fe-Pt, but Pt tends to occupy low coordination sites. An icosahedral $Fe_{72}Pt_{75}$ (close to 50:50 composition) nanoparticle having 147 atoms (~ 1.5 nm diameter) was investigated and found to phase separate into a Fe_{55} core and $(Fe-Pt)_{92}$ ordered shell. These results show that such nanoparticles prefer decahedral or icosahedral structure and a transition to bulk structure should occur at significantly higher sizes, which agrees with experiments that show a transition to bulk structure in FePt nanoparticles for sizes larger than 2.5 nm. Further *ab initio* calculations were done for the first time on Fe_3Pt type nanoparticles (soft magnetic material) embedded in FePt matrix (hard magnet) to model composites. These results revelaed enhancement in the magnetic moments in both the nanoparticles and the matrix compared with the bulk behavior of the soft and hard phases and ferromagnetic coupling.

"**Magnetic Properties of Nanoparticle Matrix Composites**"

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Abstract: The aim of the project was to develop strong permanent magnets using nanoparticles and their composites. For this an understanding of the magnetic properties of nanoparticles was also needed. Assemblies of nanoparticles can be used to develop novel exchange coupled strong magnets without using rare earths as well as for high density magnetic recording media. Some of these nanoparticles (such as Fe-Pt) can also be very interesting for catalysis. Fe-Pt is one of the most promising materials due to its large magnetic anisotropy. We carried out ab initio calculations on Fe-Pt nanoalloys (clusters and nanoparticles) to understand the atomic and electronic structure, and the magnetic behaviour. Our results revealed a tendency for Pt segregation on the surface and a preference for maximizing Fe-Pt bonds. The formation energy of the nanoalloys is the highest around 50:50 composition as also in bulk Fe-Pt, but Pt tends to occupy low coordination sites. We designed an icosahedral $Fe_{72}Pt_{75}$ (close to 50:50 composition) nanoparticle having 147 atoms (~ 1.5 nm diameter) but it phase separates in to Fe_{55} core and $(Fe-Pt)_{92}$ ordered shell. Our results show that such nanoparticles prefer decahedral or icosahedral structure and a transition to bulk structure should occur at significantly higher sizes. This agrees with experiments that show a transition to bulk structure in FePt nanoparticles for sizes larger than 2.5 nm. Further ab initio calculations have been done for the first time on Fe_3Pt type nanoparticles (soft magnetic material) embedded in FePt matrix (hard magnet) to model composites. Our results show enhancement in the magnetic moments in both the nanoparticles and the matrix compared with the bulk behaviour of the soft and hard phases and ferromagnetic coupling. We believe that our results have guided us to important factors that would help design of strong magnets as well as

some very stable nanoparticles. As the calculations on nanocomposites are very demanding, we studied superlattices of hard and soft magnetic phases to determine the optimal sizes of the hard and soft phases. Our calculations suggest that the soft phase region should be of less than ~ 2 nm size. This is in excellent agreement with very recent experiments.

Introduction:

Properties of nanomaterials depend on size, shape, and atomic structure. Often the atomic structure is size dependent and can be very different from bulk. This gives us new opportunities to develop novel materials using nanoparticles as building blocks. In this project our focus has been on magnetic properties of nanoparticles and their assemblies in the form of composites for developing strong magnets. Also such materials are interesting for magnetic recording. It is generally found that there is enhancement in the magnetic moments as the size decreases, e.g. there are about 3 μ_B magnetic moments on Fe clusters/nanoparticles (having up to around 150 atoms) [1] per atom compared with 2.2 μ_B for bulk. Alloying Fe with some suitable elements further enhances its magnetic moments due to charge transfer and hybridization. These aspects of alloying and using nanomaterials when combined together could facilitate building strong magnets. Kneller *et al.* [2] proposed a model to build strong magnets using composite materials where a soft magnet having high saturation magnetization is enveloped by a hard magnet with high coercive field. Such a composite with strong exchange coupling could exhibit large coercivity as well as high magnetic moments. Following this idea, experiments [3-6] on composites with a variety of combinations such as SmCo/FeCo [7], PrCo/Co [8], $Fe_3B/Nd_2Fe_{14}B$ [9], SmCo/NdCo [10], NdFeB/Fe [11], and SmCo/Fe [11] have been performed, but theoretical work is very little due to the complexity of the system. Calculations on $SmCo_5/Co(Fe)$ [12], and $Sm_2Fe_{17}N_3/Fe_{65}Co_{35}$ [13] multilayers supported the experiments. Skomski *et al.* [13] proposed that the energy product of a composite can be improved with nanoscale combination of a soft magnet phase and oriented hard phase having cellular and disordered structures. Experiments by the group of Sun [14-16] on magnetic nano-composites using self-assembly of nanoparticles without having rare earth elements, supported the work of Kneller *et al.* [2] and Skomski *et al.* [13]. It has been found that the $3d/5d$ combination of transition metals such as FePt alloy and Fe_3O_4 nanoparticles coalesce subject to external temperature and leads to the formation of two distinct phases namely face centred tetragonal (FCT) FePt and face centred cubic (FCC) Fe_3Pt, in which Fe_3Pt is a soft magnet enveloped by a hard magnet FePt [14-16]. The composite $FePt-Fe_3Pt$ has a high energy

product (20.1 MGOe) compared to a single phase FePt (14.7 MGOe) [16, 17]. Experiments on core-shell [18] or bi-magnetic [16] nanoparticles led to conclusions in similar direction. Among the many possibilities that have been explored for the high density magnetic recording materials with large value of K_u are $SmCo_5$ with $K_u = $ 11-20 x 10^7 erg/cm^3 for the minimum stable particle size of 2.45 nm, FePt with $K_u = $ 6.6-10 x 10^7 erg/cm^3 with the minimum stable particle size of 3.05 nm, and $Nd_2Fe_{14}B$ with K_u value of 4.6 x 10^7 erg/cm^3 for the minimum particle size of 3.7 nm [19]. FePt is found to be the best due to its magnetic and chemical stability with high magneto-crystalline anisotropy. Moreover, it is desirable to develop strong magnets without rare earth elements. Fe-Pt nanoparticles are also projected to be used in future commercial magnetic storage hard disks. We therefore devoted our efforts to study the Fe-Pt based magnetic materials, both nanoparticles and nanoparticle-matrix composites as well as superlattices.

We considered small clusters as models to understand the alloying behaviour at the nanoscale in Fe-Pt clusters/nanoparticles and the evolution of the magnetic behaviour from an atom towards bulk. Calculations have also been done on Fe_3Pt and FePt type nanoparticles having up to around 200 atoms with the atomic structure taken as a bulk fragment as well as by considering other structures such as decahedral and icosahedral. In each case spin isomers have been studied. The Fe_3Pt-FePt nanoparticle-matrix composites have been studied by considering a supercell of FCC type structure in which Fe_3Pt nanoparticles were embedded in a FePt matrix. Variations in the size of the matrix and the nanoparticles have been studied. We considered supercells with up to 500 atoms. These *ab initio* calculations with full optimization as well as calculation of the magnetic properties are very demanding and for larger cells the number of atoms to be included in the calculations can be a few thousand considering a few nm thick nanoparticles. Therefore further studies were made on superlattices. We considered FePt layers for hard phase while for soft phase FeCo, Fe, as well as Fe_3Pt layers were taken. The thicknesses of the layers were varied and an optimal size of the soft phase to achieve good anisotropy as well as high magnetization for developing permanent magnets has been found to be less than about 2 nm. This is in excellent agreement with the recent experiments on thin films as well as on nanoparticle composites. In the following sections we describe our method of calculations and significant results on clusters, nanoparticles, matrix-nanoparticle composites, and superlattices.

Method of Calculation:

The calculations have been performed using VASP code [20] with projector augmented wave (PAW) pseudopotentials [21] and spin-polarized generalized gradient approximation of Perdew *et al.* (PBE) [22] for the exchange-correlation energy. The pseudopotentials have been generated using scalar relativistic method. Several atomic structures of small Fe-Pt clusters have been optimized for each composition of Fe-Pt and their spin isomers have been studied to find the magnetic moments of the lowest energy structures. Further, the heat of formation of the clusters has been calculated from $\Delta H = E(Fe_nPt_m) - (n/N) E(Fe_N) - (m/N) E(Pt_N)$ where $N = n + m$. For nanoparticles having of the order of 100 atoms, it is a difficult task to obtain the lowest energy structure as a very large number of possibilities exist and many isomers may lie close in energy. We have used the results of the calculations on small clusters as a guide to understand the atomic structures and properties of nanoparticles. We studied a few isomers for each size of the nanoparticles with N = 38, 79, 116, 140, and 172 atoms and also focussed our attention on nanoparticles with 55 and 147 atoms which become icosahedral. Then we explored the magnetic isomers as well as Pt segregation and ordering. Further, the nanoparticle-matrix composites have been studied by considering a 4x4x4 FCC supercell (256 atoms) as well as a 5x5x5 supercell with 500 atoms. We considered 2x2x2 and 3x3x3 Fe_3Pt type nanoparticles in FePt matrix. The atomic structure and lattice parameters have been fully optimized without imposing any symmetry. In order to further find the optimal size of the hard and soft magnetic phases, calculations have been performed on FePt/FeCo, FePt/Fe, and FePt/Fe_3Pt superlattices. We also included effects of spin-orbit coupling to study magnetic anisotropy energy. In the following we discuss significant results.

Results and Discussion:

1.   Atomic structure and magnetic behaviour of small Fe-Pt clusters

We studied small clusters of Fe_nPt_m with N = n + m ranging from 2 to 10 as model to understand the atomic and electronic structure, magnetic behavior, and charge transfer effects in nanoalloys. The lowest energy structures and some low lying isomers for N = 2-7 are shown in Fig. 1. The lowest energy isomers of Pt clusters are generally planar [23] in this small size range while those of Fe clusters have close packed structures. In Fe-Pt clusters there is a tendency to maximize FePt bonds as energetically such unlike bonds are

more favorable compared to Fe-Fe and Pt-Pt bonds. We calculated the heat of formation (ΔH), second order difference in energy ($\Delta_2 = E(Fe_{n-1}Pt_{m+1}) + E(Fe_{n+1}Pt_{m-1}) - 2\ E(Fe_nPt_m)$) and the binding energy to find the trends.

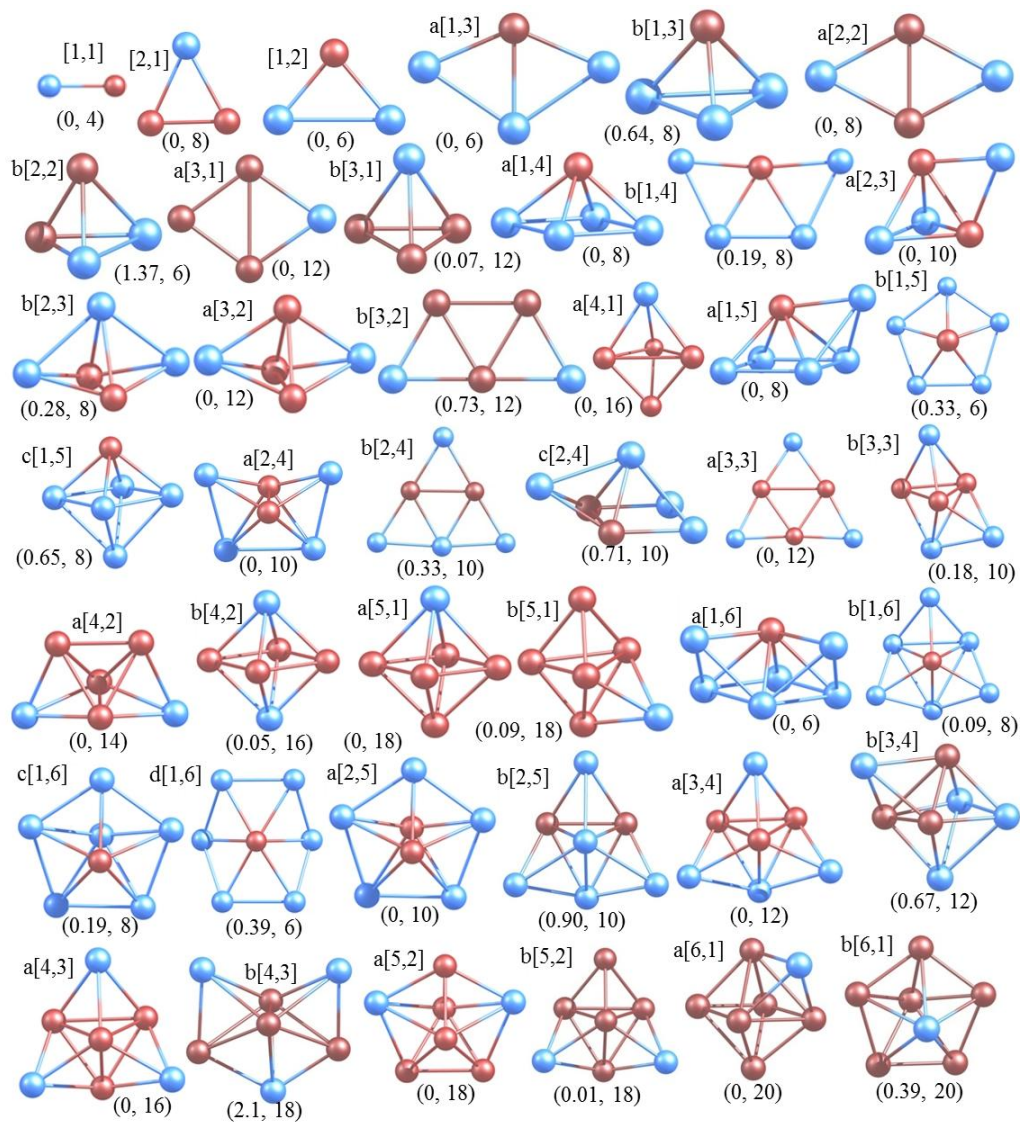**Fig. 1.** Low lying isomers of Fe-Pt clusters for N = m + n = 2-7. Here x[m,n] refers to isomers x = a, b … in increasing order of energy for a cluster with m (n) Fe (Pt) atoms. The numbers in brackets below the structures refer to the energy (eV) relative to the lowest energy isomer and the magnetic moment (μ_B). Red (blue) balls represent Fe (Pt) atoms.
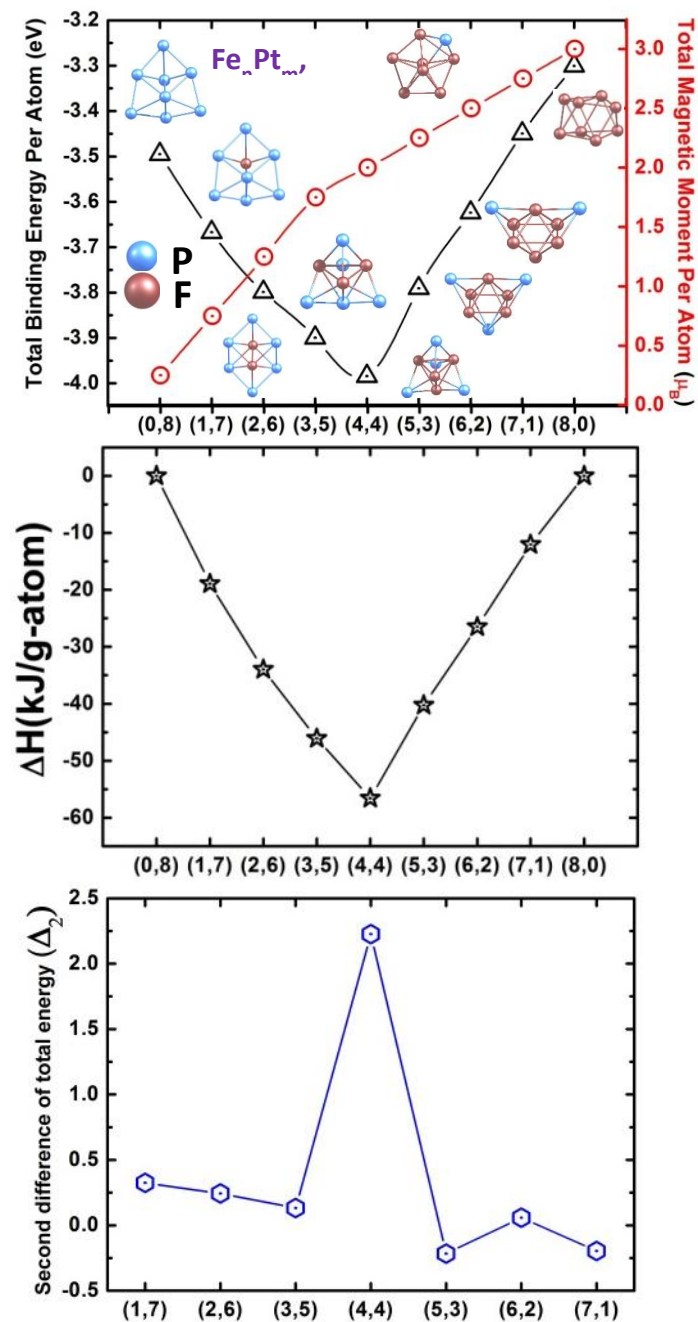
Fig. 2. The total binding energy (eV/atom) along with the total magnetic moment (μ_B) per atom, heat of formation (ΔH), and the second order difference of total energy (Δ_2) for (Fe_nPt_m) cluster for n + m = 8.

The key findings are as follows. It is observed that clusters with almost equal compositions of Fe and Pt atoms have the lowest energy. Fe_2Pt_2, Fe_4Pt_4 and Fe_4Pt_6 clusters are the best from the point of view of the binding energy, ΔH, and Δ_2 calculations. We have shown in Fig. 2 the results for N = 8 and from the values of Δ_2, we find that Fe_4Pt_4 stands out. Fe-Pt bonds with Fe (Pt) having high (low) coordination are preferred in the lowest energy

structures. The magnetic moments increase systematically by $4\mu_B$ when a pair of FePt or a single Fe atom is added to an existing cluster, whereas the increase is by $2\mu_B$ upon the addition of a single Pt atom. As shown in Fig. 3, the magnetic moment of Fe atoms reaches a maximum of about $3.5\mu_B$ and in some cases even up to $3.8\ \mu_B$ which is much higher than the values in bulk Fe-Pt alloys. Also the magnetic moments on Pt atoms have larger value of about $0.7\ \mu_B$ per atom compared with $0.34\ \mu_B$ in bulk. The magnetic moments on Fe atoms tend to decrease as the number of Fe atoms increases. Therefore nanomaterials are promising to form strong magnets without using rare earth elements.
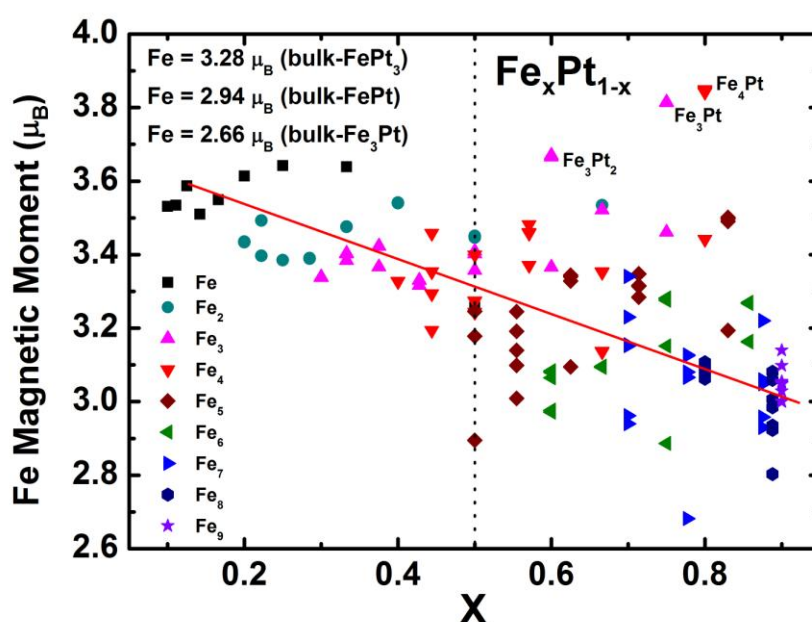

Fig. 3. Magnetic moments on Fe atoms in Fe_mPt_n clusters. The points denoted by different symbols correspond to clusters with one, two, three, ……, nine Fe atoms. x is the fraction of Fe atoms in the nanoalloy cluster. Also mentioned are the magnetic moments in three bulk phases. The magnetic moments have a decreasing tendency from a high value for small number of Fe atoms to lower values for large number of Fe atoms in Fe-Pt clusters. The line is drawn to aid eye. The magnetic moments are generally higher in clusters than in the corresponding bulk phase.

The charge on each Fe atom is depleted by about 0.7e and the charge on Pt atoms is in excess of about 0.5e, indicating charge transfer from Fe to Pt atoms which is similar to bulk FePt. The charge transfer helps to increase magnetic moments on Fe atoms.

2.   Segregation and ordering on the surface of Fe-Pt nanoparticles

Experiments suggest that $L1_0$ structure is achieved in Fe-Pt nanoparticles only in the size range of greater than 2.5 nm [24,25]. Earlier theoretical studies on Fe-Pt nanoclusters were on selected sizes with ordered, disordered, and core-shell arrangements by considering cuboctahedral, icosahedral, and decahedral geometries [24-29]. It has been reported that an icosahedral isomer with alternating Fe/Pt shells and core-shell structures are energetically lower in energy [24,28,29]. Bulk Fe has 4.288 eV/atom cohesive energy which is smaller than the cohesive energy of Pt (5.854 eV/atom [30]), but due to the larger size of Pt atom, the surface energy of Pt is lower than for Fe. This could lead to segregation of Pt atoms on the surface as also we find in small clusters. The bulk formation energies show that Fe-Pt bonds are favorable [31] similar to what we also found in clusters.

We considered FePt and Fe_3Pt type nanoparticles with 38, 55, 79, 116, 140, 147, and 172 atoms. The icosahedral, decahedral, and cuboctahedral arrangements have been considered along with some spin isomers. An interesting finding has been the instantaneous transformation of a bulk cubic fragment with 63 atoms to an icosahedral structure with 8 atoms capping a 55-atom cluster. As 55 atoms form a nice icosahedral structure, we removed the extra atoms from the surface and further rearranged Pt atoms from inside the nanoparticle to the surface. This lowered the total energy of the 55-atom nanoparticle and suggested that segregation of Pt on the surface is favored. Also relativistic effects are likely to favor Pt on the surface so that the kinetic energy of electrons can be lowered. In the size range of around 55 atoms, Fe clusters favor icosahedral structure and an icosahedral core of Fe seems to be the best. Further, we have found ordering of Fe and Pt atoms on the surface of an icosahedral nanoparticle to be energetically favorable. This is again positive for the stability. Fe core enhances the stability and the magnetic moments. Note that pure Fe clusters in this size range have about 3 μ_B magnetic moments/atom. These 55-atom nanoalloy clusters/nanoparticles shown in Fig. 4 incorporate more than one favorable aspect, namely (1) Fe nanocluster at the core that will have high magnetic moments, Pt enrichment on the surface, and (3) ordering of Fe and Pt atoms on the surface. The core-shell type FePt and Fe_3Pt decahedral structures are lower in energy for nanoparticles with 116 atoms over icosahedral (taken as reference), cuboctohedral, and $L1_0$ ordered structures, while icosahedral structures are the lowest in energy for nanoparticles with N = 140, 147, and 172.
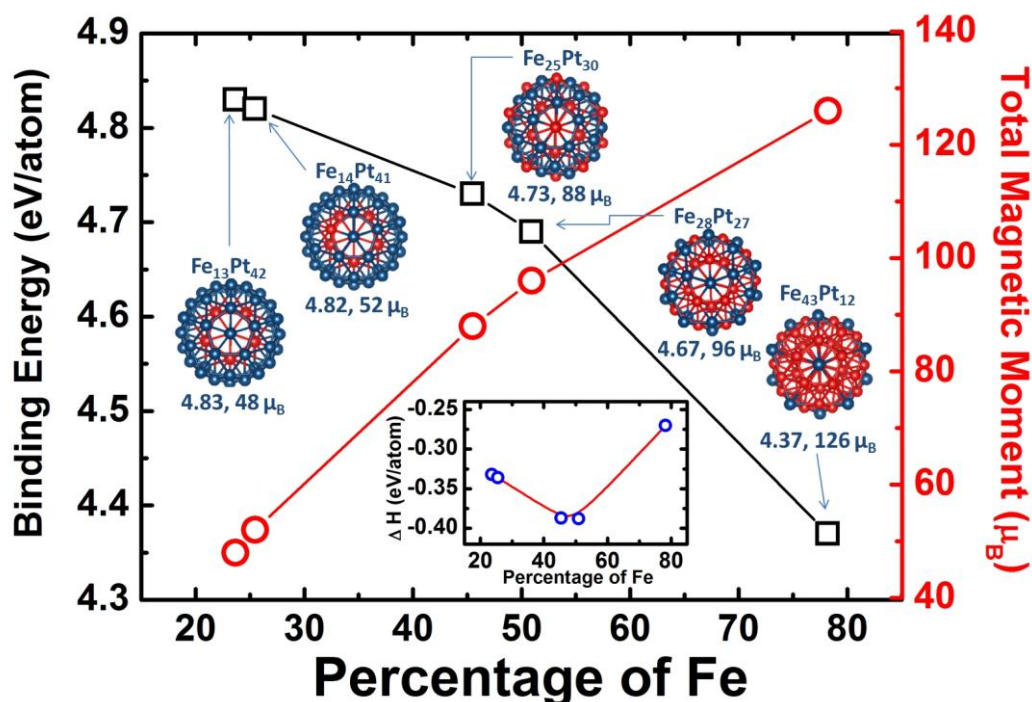
Fig. 4: Plots of the binding energy per atom and the total magnetic moments of different 55-atom Fe-Pt nanoparticles with increasing number of Fe atoms namely $Fe_{13}Pt_{42}$, $Fe_{14}Pt_{41}$, $Fe_{25}Pt_{30}$, $Fe_{28}Pt_{27}$, and $Fe_{43}Pt_{12}$ lowest energy isomers. Brown (blue) balls represent Fe (Pt) atoms. Each isomer is indicated by the arrows with their respective binding energy in eV/atom and the magnetic moments. Inset shows the heat of formation (ΔH) of nanoparticles with different compositions. The $Fe_{28}Pt_{27}$ nanoparticle with nearly equiatomic composition has the largest ΔH whereas the nanoparticle $Fe_{25}Pt_{30}$ has a slightly less value.

3.   The finding of $Fe_{75}Pt_{72}$ nanoparticle

It is known [26] that Fe clusters have icosahedral structure (albeit distorted) for the lowest energy isomers in the size range of up to around 147 atoms. Also in this size range there are large magnetic moments (~ 3 per atom on Fe clusters). We found that Fe-rich Fe_3Pt nanoparticles transform to icosahedral structure instantaneously while bulk fragments of FePt remain in cuboctahedral structure. However, an icosahedral structure with Pt segregation on the surface is lower in energy in this size range. We designed a $Fe_{75}Pt_{72}$ nanoparticle with nearly 50:50 composition of Fe and Pt, but it phase separates in to Fe_{55} core and $Fe_{20}Pt_{72}$ ordered shell as shown in Fig. 5. All the Pt atoms are on the surface. There is high magnetic moment on Fe atoms compared to bulk Fe ($2.2\mu_B$) and FePt ($2.94\mu_B$). These results suggest that larger size nanoparticles are needed to have bulk

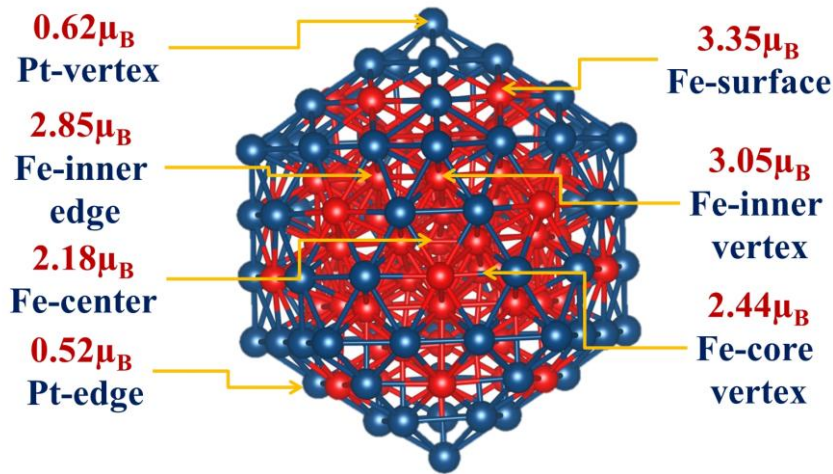structure of nanoparticles and to make anisotropic structures.

Fig. 5: The magnetic moments on different Fe and Pt atoms in icosahedral $Fe_{75}Pt_{72}$ nanoparticle for the lowest energy isomer. The central Fe atom has lower magnetic moments due to compression in icosahedral structure.

4. FePt-Fe₃Pt matrix-nanoparticle composites

The magnetic properties of composites with Fe_3Pt type nanoparticles (soft magnet) embedded in Fe-Pt matrix (hard magnet) depend on 1) the thickness of the shell (matrix) as well as the size of the nanoparticles and 2) the lattice parameters and distortions as well as the bonding nature/electronic structure at the interface that affects the nanoparticle-matrix magnetic interactions [2,13,14,32].

There are no reports on soft-hard nanoparticle-matrix composites using density functional theory calculations to understand the dependence of exchange-coupling between soft and hard phases and interface conditions. For the first time we have conducted a full-fledged *ab initio* calculation on soft-hard magnetic nanoparticle-composites to understand the size and interface effect of core as well as matrix on magnetic properties. We modeled Fe_3Pt-FePt soft-hard nanoparticle-matrix magnetic nano-composites by a supercell having up to 500 atoms to understand the structural, electronic, and magnetic properties. The experimental lattice parameter of bulk Fe_3Pt in FCC structure is $a = 3.75$Å while bulk FePt is slightly anisotropic and in FCT structure its cell dimensions are $a = b = $

3.852 Å and $c = 3.713$ Å [33].

Starting with a FCC structure, we considered 2x2x2 Fe_3Pt nanoparticle embedded in 4x4x4 (about 1.5 nm) as well as 5x5x5 (about 2 nm) FePt matrix and 3x3x3 Fe_3Pt nanoparticle in 5x5x5 matrix (see Fig. 6) in order to study the effects of the variation of the nanoparticle size and the matrix. These sizes are small compared to an optimal size of about 4 nm (see later) for the supercell that will have about 5000 atoms and which is difficult to treat from *ab initio* calculations, but we hope to capture the underlying phenomena. Hereafter we call nxnxn nanoparticle in mxmxm matrix as nNmM. The 2N4M and 2N5M composites have the same size of the nanoparticle but different thickness of the matrix while 2N5M and 3N5M nano-composites have different sizes of the nanoparticles but the same thickness of the matrix. The overall compositions of 2N4M, 2N5M, and 3N5M nano-composites are $Fe_{155}Pt_{101}$ with $Fe_{51}Pt_{12}$ nanoparticle and $Fe_{104}Pt_{89}$ matrix, $Fe_{258}Pt_{242}$ with $Fe_{44}Pt_{12}$ nanoparticle and $Fe_{214}Pt_{230}$ matrix, and $Fe_{314}Pt_{186}$ with $Fe_{136}Pt_{36}$ nanoparticle and $Fe_{178}Pt_{150}$ matrix, respectively. The composition of the matrix in all the cases is close to equal fraction of Fe and Pt while for the nanoparticles, it is close to Fe_4Pt but the phase is Fe_3Pt only. The excess Fe is due to the fact that full 2x2x2 fragment is considered unlike in a unit cell. The optimized 3N5M supercell is shown in Fig. 6.

The optimized structures show that *the FePt matrix has face centred tetragonal (FCT) structure and it induces similar tetragonal distortion in the Fe_3Pt nanoparticle as well.* The c/a ratio of the supercell is close to 0.96 as also in bulk FePt. The structural anisotropy makes the magnetic spin align along the easy axis in Fe_3Pt soft magnet which is also the easy axis for FePt matrix. This behavior would lead to higher coercivity and high energy product in nano-composites with significantly reduced (only 37-40%) Pt content. Therefore soft-hard composite is a good way to make strong magnets. We also studied the effect of structural anisotropy in bulk Fe_3Pt to obtain magnetic anisotropy energy (MAE) by varying c/a ratio from 0.99-0.95 keeping the volume fixed. The calculated MAE is found to vary from 0.22 to 0.50 meV per formula unit, which is ~10-20% of the bulk FePt value (2.07 meV per formula unit).
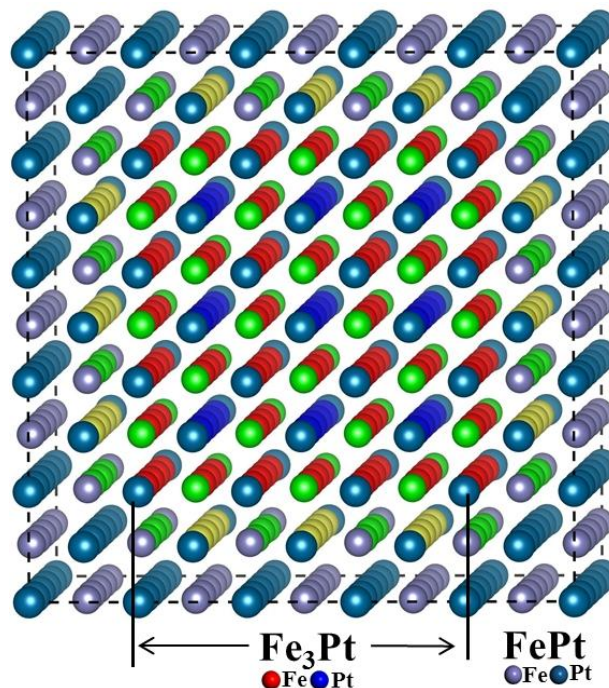
Fig. 6.   The optimized atomic structure of FePt-Fe$_3$Pt matrix-nanoparticle composite in FCC type structure (supercell) has tetragonal distortions. The overall composition is Fe$_{51}$Pt$_{12}$ (nanoparticle) and Fe$_{104}$Pt$_{89}$ (matrix). Another composition has also been studied in which a different distribution (Fe$_{44}$Pt$_{18}$ and Fe$_{102}$Pt$_{92}$) of atoms in the nanoparticle and matrix, respectively, is taken.

Figure 7 shows the results of the Bader analysis of the local magnetic moments and charge on each atom in the nano-composites. The local magnetic moments are higher on a large number of atoms compared to 2.95 μ_B (0.34 μ_B) and 2.65 μ_B (0.34 μ_B) on Fe (Pt) in bulk FePt and Fe$_3$Pt, respectively. The magnetic moments have the highest values in the edge region (part of the FePt matrix excluding the interface atoms in the supercell) and they decrease towards the value in Fe$_3$Pt nanoparticle via the interface region. There is charge transfer from Fe atoms to Pt atoms as the total charge on Fe (Pt) atoms is < 14e (> 10 e). The overall trend of the charge on each atom of the nano-composite is increasing in going from the edge region to the nanoparticle region. The charge on Fe atoms in the edge region is more than in bulk FePt as less charge is transferred to Pt atoms, but still the magnetic moments are higher on many atoms. This indicates the role of hybridization between the Fe and Pt states as also observed for free Fe-Pt nanoparticles and the importance of quantum confinement and interface effects. The charge on Fe atoms in the nanoparticle region is higher than in bulk Fe$_3$Pt due to higher Fe concentration and less charge transfer per Fe atom to Pt atoms. The charge on Pt atoms approaches the value

(11.03 e) in bulk Fe_3Pt.

In the nanoparticle region, the magnetic moments on all the Fe atoms in the nano-composites are generally enhanced to up to about 3 μ_B compared with 2.65 μ_B in bulk Fe_3Pt, while on Pt atoms the values lie in a narrow range of 0.33 to 0.43 μ_B which is also an enhancement compared with the bulk Fe_3Pt value. The reduction (increase) of charge on Fe (Pt) atoms in the nanoparticle region is ~0.4e (~0.9e). We conclude that there is a significant enhancement in the magnetic moments on Fe and Pt atoms in all the regions of the nano-composites compared with the values for the constituents.
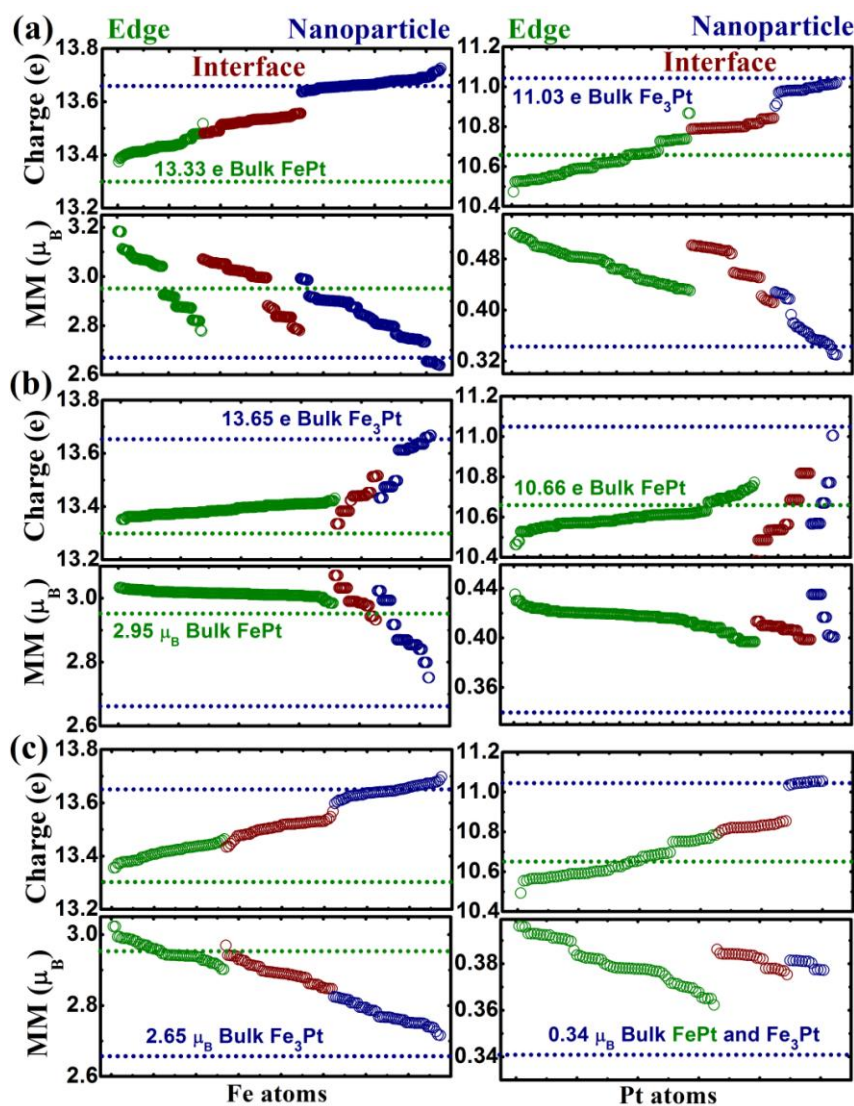

Fig. 7. Charge (upper panel in each plot) and magnetic moments (MM) (lower panel in

each plot) on Fe (left panels) and Pt (right panels) atoms of the (a) 3N5M, (b) 2N5M, and (c) 2N4M nano-composites. Atoms are arranged from edge region (green circles) to interface region (maroon circles) to nanoparticle region (blue circles). Charge on Fe (Pt) atoms is less (more) than 14 e (10 e) and indicates transfer of charge from Fe to Pt atoms.

We further calculated the maximum energy product for the nano-composites from $(BH)_{max} = \frac{1}{2}\mu_0(M_s)^2$, where M_s is the saturation magnetization defined as the ratio (M/V) of the total magnetic moments (M) to the total volume (V) and μ_0 is the permeability of free space. It is desirable to increase M and simultaneously reduce V for large $(BH)_{max}$. The values of M_s for bulk FePt and Fe$_3$Pt are 0.117 and 0.160 μ_B/Å^3, respectively. Note that the volume of FePt hard magnet (56.18 Å^3 per unit cell) is slightly higher than 51.97 Å^3 for Fe$_3$Pt due to higher content of Pt which has larger atomic volume than Fe. The higher magnetization in nano-composites is partly due to the increased Fe content compared with FePt and the reduced volume (reduction being 3.5%, 0.5%, and 3.2% for 3N5M, 2N5M, and 2N4M nano-composites, respectively) compared with bulk FePt. 3N5M and 2N4M nano-composites have high magnetization of 0.145 and 0.138 μ_B/Å^3 compared to 0.117 μ_B/Å^3 for FePt. The calculated M_s for 2N5M nano-composite is lower (0.125 μ_B/Å^3) due to higher Pt content. These results suggest that we can achieve the desired result of reduced Pt content and higher magnetic moments in nano-composites. The calculated $(BH)_{max}$ of 71.8, 52.9, and 65.7 MGOe, respectively, for 3N5M, 2N5M, and 2N4M nano-composites is quite high compared with the calculated value of 46.8 MGOe for bulk FePt. Our values are also comparable or higher than the highest reported experimental value of ~50 MGOe [10-15] for Fe$_3$Pt-FePt composites and 57.6 MGOe for the strongest magnet, Nd$_2$Fe$_{14}$B. In order to further understand the variation of the magnetic properties with size, we studied superlattices and the results are discussed in the following.

5. FePt/FeCo superlattices

Thin films of FePt/Fe, FePt/Co, and FePt/FeCo have been realized [34]. Liu *et al*. [35] obtained 54 MGOe for aligned and exchange-coupled FePt based films. For FeCo/FePt superlattices, Hong *et al*. [36,37] obtained $(BH)_{max}$ to be ~65 MGOe from *ab initio* calculations considering L1$_0$-ordered FePt and FCC type FeCo. However, the actual crystal

structure of FeCo is B2-type. The latter has been recently confirmed from experiments [38] in which B2-type FeCo was epitaxially grown on $L1_0$-ordered FePt layers by rotating FeCo unit cell by 45° with respect to that of FePt layers. Ishio and coworkers [39] also developed FePt/FeCo bilayers and reported higher anisotropy field, magnetic anisotropy energy, and saturation magnetization in comparison to FePt/Fe and FePt/Co bilayers. The optimal thickness of the FeCo layers has been found to be less than 2 nm to produce high anisotropy field. Also the easy axis of FeCo is normal to the film plane if its thickness is < 3 nm. In another experiment [40] on $FePt/Fe_3O_4$ nanoparticle composites, the optimal thickness of the soft phase nanoparticles to achieve high energy product has been also found to be less than 2 nm. We study the magnetic behavior of $Fe_{50}Pt_{50}/Fe_{50}Co_{50}$ superlattices with $L1_0$-ordered FePt and B2-type FeCo layers to obtain the structural anisotropy, $(BH)_{max}$, magnetic anisotropy energy (MAE), and the anisotropy field by varying the thicknesses of the hard (FePt) and soft (FeCo) magnetic layers. Our results suggest that the large uniaxial anisotropy constant, K_u as well as magnetization is achieved when the thickness of the soft magnetic phase is less than 2 nm which is in close agreement with experiments.

We constructed m-n superlattices by arranging m layers of FePt and n layers of FeCo in such a way that the $L1_0$ ordered FePt layers are rotated by 45 ° with respect to B2-FeCo layers so that the nearest neighbour in-plane distance in FePt layers matches with the lattice parameters of the B2-type FeCo layers. We considered m = 4, 6, and 8 and varied n from 2 to 2m so that the stoichiometries of FePt and FeCo layers remained intact. Figure 8 shows supercells for (a) 4-2, (b) 4-4, (c) 4-6, and (d) 4-8 superlattices. Similar models have been designed for other superlattices.
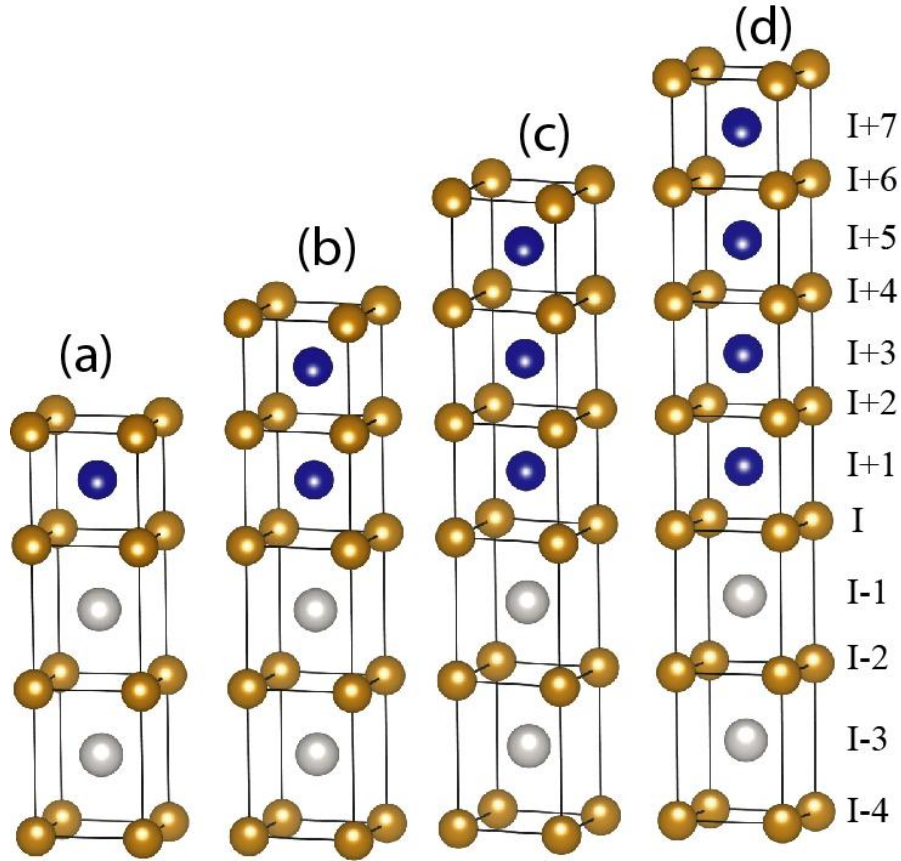
Fig. 8. Ball and stick models of $(FePt)_m/(FeCo)_n$ superlattices with m layers of FePt in $L1_0$ structure and n layers of FeCo in B2 structure. Brown, white, and blue balls represent Fe, Pt, and Co atoms, respectively. (a), (b), (c), and (d) show supercells for m-n = 4-2, 4-4, 4-6, and 4-8 superlattices, respectively. The FePt layers are rotated by 45° with respect to FeCo layers. The symbol I refers to the interface layer.

The interlayer separations d_{FePt} and d_{FeCo} and the in-plane lattice parameters $a = b$ in the optimized structures vary as shown in Figs. 9 and 10(a), respectively. In general for a given value of n, a is reduced if the number of FePt layers is increased and for a given value of m, a increases towards the value for FeCo as n is increased. This is because the in-plane nearest neighbour bond length in FePt (2.726 Å) is slightly shorter than the lattice constant of bulk FeCo (2.841 Å). The interlayer separations d_{FePt} and d_{FeCo} show an oscillatory behavior with the largest contraction (expansion) for FePt (FeCo) layer at the interface. For the next layer, d_{FePt} (d_{FeCo}) increases (decreases) towards the bulk value in all cases. Thereafter d_{FeCo} shows only a small variation around the value of 1.46 Å (bulk value 1.42

Å), but oscillatory behavior continues in the case of d_{FePt}. These results show that *significant anisotropy is created in FeCo by the formation of the superlattice as we also found in composites*. When the number of FePt layers is much larger than the FeCo layers such as in 8-2 superlattice, d_{FePt} tends to approach the bulk FePt value (1.925 Å) and the anisotropy in FeCo layers is the highest among all the cases we have studied. But it results into a lower value of the average magnetization and therefore lower energy product. To enhance average magnetization, we need to increase the number of the FeCo layers. For the FeCo rich cases such as the 4-6 superlattice, the anisotropy is on the lower side but it is large enough and fulfils the requirement of high magnetization and high enough anisotropy for applications as we shall discuss later. In other cases such as 6-10 and 8-12 superlattices, there is also reasonably high anisotropy in FeCo layers. Accordingly, such superlattices are promising for permanent magnets.
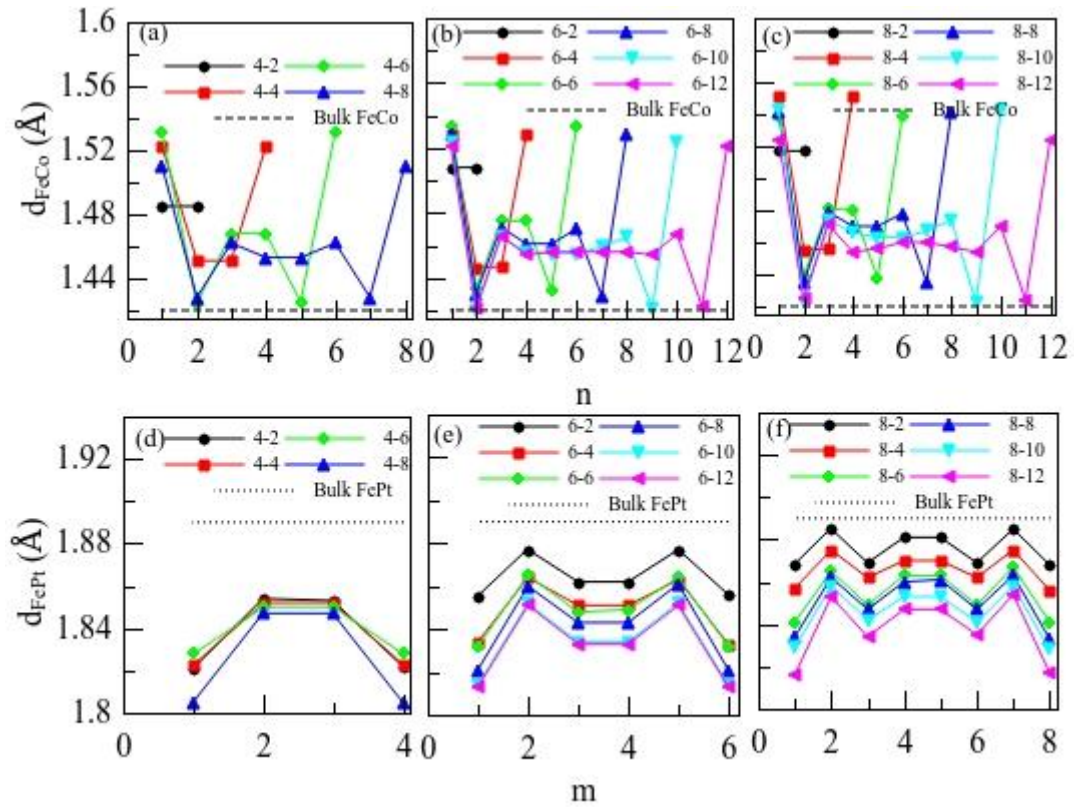

Fig. 9. Variation in the interlayer separations of FeCo (FePt) for (a) and (d) 4 FePt layers, (b) and (e) 6 Fept layers, and (c) and (f) 8 FePt layers as n (m) is varied. Black dashed line indicates the interlayer separation of bulk FeCo (FePt).

The average magnetic moments in bulk FePt and bulk FeCo are calculated to be 1.62

μB/atom and 2.24 μB/atom, respectively. The Bader charge analysis reveals that the local magnetic moments on Fe atoms in bulk FePt and bulk FeCo are 2.90 μB and 2.74 μB, respectively. The local magnetic moment on Pt (Co) atoms is 0.34 μB (1.75 μB) in bulk FePt (FeCo). The high magnetic moment on Fe atoms also arises as there is 0.67 e⁻ charge transfer from Fe to Pt atoms in bulk FePt while in the case of FeCo only 0.16 e⁻ is transferred to Co resulting in a lower value. In the case of superlattices the magnetic moments are modified due to structural changes. For the 4-2 superlattice, the average magnetic moment is 1.885 μB/atom which is higher than in bulk FePt. It increases further with FeCo thickness and the highest average magnetic moment (2.10 μB/atom) is obtained for the 4-8 superlattice among all the cases we have studied. This is ~30% higher compared with the value in bulk FePt. From the Bader charge analysis the local magnetic moment at the interface Fe (Fe_I) atoms that are nearest to both Co and Pt atoms is 2.87μB. These Fe atoms give 0.44 e charge to the neighboring Co and Pt atoms whereas Fe atoms of FePt nearest to the interface (Fe_{I-2}) have 3.05 μB magnetic moments in 4-2 superlattice and there is 0.68 e charge transfer from Fe to the neighboring Pt atoms. The magnetic moments on Fe_I and Fe_{I-2} atoms are higher than on Fe in bulk FeCo and FePt, respectively. The highest value of the magnetic moments 3.11 μB (Fe_{I-2}) and 2.94μB (Fe_I) is obtained in 4-8 superlattice. However, beyond the interface region, the magnetic moments decrease and tend to attain the bulk value.
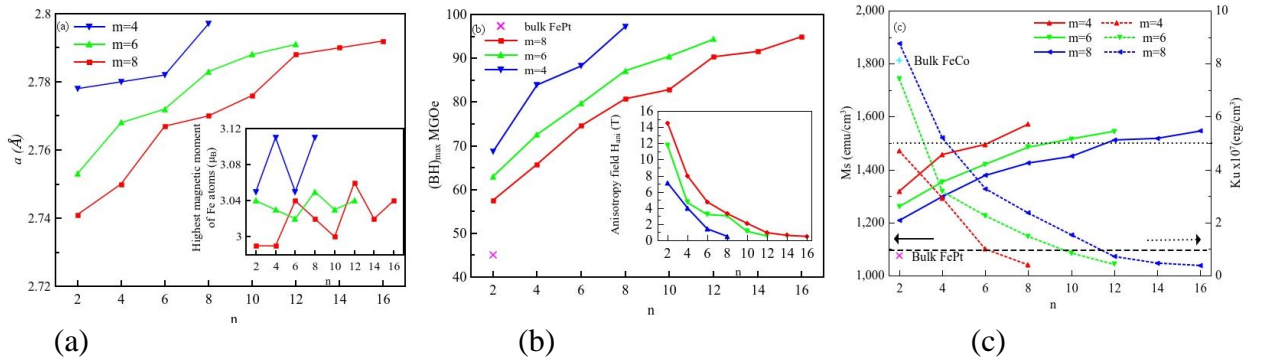

FIG. 10: (a) The in-plane lattice parameter a of the $(FePt)_m/(FeCo)_n$ superlattices. The inset shows the highest local magnetic moments on Fe atoms for the different superlattices. (b) Maximum energy product for different superlattices with the inset showing the anisotropy field, and (c) variation in magnetization as well as K_u.

The magnetization (magnetic moments per unit volume, M_s) increases with the number of FeCo layers which have lower average volume/atom and decreases with the increase in the number of FePt layers that have lower magnetic moments and higher average volume. Figure 10 (c) shows that M_s of 4-2 superlattice is 1,318.53 emu/cm^3 and it increases with FeCo thickness and becomes the highest for 4-8 superlattice. The magnetization of 6-2 and 8-2 superlattices is calculated to be 1,260.68 emu/cm^3 and 1,208.14 emu/cm^3, respectively. The maximum energy product (BH)$_{max}$ (Fig. 10(b)) shows the same trend as M_s. It increases with n, the number of FeCo layers and decreases with m, the number of FePt layers. The highest value of (BH)$_{max}$ is 97.22 MGOe and it is obtained for the 4-8 superlattice among all the systems we have considered. For 6-2 and 8-2 superlattices, the values are 62.96 MGOe and 57.53 MGOe, respectively. It is important to note that while (BH)$_{max}$ increases with the number of the soft magnet layers, the value of MAE decreases as shown in Fig. 10 (c). A large value of MAE is important for developing hard magnets and this puts a limit on the thickness of the soft magnetic layers. We calculated K_u for the different FePt/FeCo superlattices by varying m and n and the values are shown in Fig. 10(c). The value of K_u for the 4-2 superlattice is 4.7x10^7 erg/cm^3 and it decreases with the increase in the thickness of the soft phase. Similarly large thickness of FePt brings about larger K_u and smaller M_s. A larger K_u suppresses the superparamagnetic fluctuations of magnetizations and withholds demagnetization. As a result it holds the information for longer period. In general, K_u of the order of 10^7 erg/cm^3 is desirable. Therefore, it is prerequisite to determine the thicknesses of the two phases. From Fig. 10(c), it is seen that for superlattices with m = 4, 6 and 8, the largest number of FeCo layers is n = 6, 10, and 12, respectively, to yield K_u of the order of 10^7 erg/cm^3. Therefore, we can predict that the optimum thickness of the soft phase is less than about 2 nm for the superlattice to work as a good permanent magnet and it also puts a limit on the thickness of the hard magnetic phase and it should also be about 1-2 nm in order to save the hard magnetic material. Also we calculated the anisotropy field $H_{ani} = 2K_u/M_s$ which is the field required to demagnetize the system or flip the magnetization directions. It is found that the suggested thicknesses of the soft and hard phases will imply anisotropy field to be about 1 T (Fig. 10(b)). Thus, our extensive study brings out the maximum energy product ~ 90 MGOe and Ku ~10^7 erg/cm^3 as well as anisotropy field H_{ani} >1T. These results are very encouraging and are in agreement with recent experiments. Our results also give support to earlier model

calculations. It would be desirable to extend this study further on larger nanoparticles to see if bulk-like ordering sets in in nanoparticles and if segregation of Pt on the surface continues. Out results on nanoparticles are also important for catalysis. Most studies on allot catalysts are using slab calculations but experiments are on nanoparticles. An important step would be to extend these studies to understand enhanced catalytic activity on nanoparticles like FePt.

Summary

We have studied Fe-Pt based clusters, nanoparticles, nanoparticle-matrix composites, and superlattices. Our calculations have given several indications which we think would help to design strong magnetic materials without rare earths. We find enhancement of magnetic moments on Fe and Pt in nanoparticles as well as in nanoparticle-matrix composites and this aspect can be exploited to develop strong magnets. Furthermore our results would also be interesting for catalytic properties of nanoparticles. We have performed for the first time ab initio calculations on magnetic composites of soft and hard phase magnetic materials and understood the variations in atomic structure and magnetic behavior as well as charge transfer effects. This will help to understand experiments on these materials. However, such calculations are difficult to perform on large systems. Therefore we studied superlattices to understand further the effects of interface and thickness of the soft and hard phases. Our results have given optimal thickness (size) of the soft magnetic phase which should be less than about 2 nm. This also means that the hard phase should of 1-2 nm size. This is very interesting as one can not only achieve good permanent magnets without rare earths, but also by reducing the Pt content. As the ordering in these systems is ferromagnetic, we did not need to take two nanoparticles in a matrix and study interaction between them.

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

I. In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a) papers published in peer-reviewed journals,

1. B.L. Chittari and Vijay Kumar, Ab Initio Studies of Segregation, Ordering, and Magnetic Behavior in $(Fe-Pt)_n$, n = 55 and 147: Design of $Fe_{75}Pt_{72}$ Nanoparticle, J. Phys. Chem. C asap (2015) (invited)

b) papers published in non-peer-reviewed journals or in conference proceedings

c) conference presentations

1. Vijay Kumar, **Invited Lecture**, *Ab initio studies of atomic structure and magnetism in Fe-Pt nanoalloys,* China-Europe International Workshop on Alloy Nanoparticles, Beijing Nov. 17-21, 2013

2. Vijay Kumar, **Plenary Talk**, Atomic structure and magnetism in Fe-Pt nanoalloys, EU COST Action MP0903 *April 5-9, 2014* "NANOALLOY" *Santa Margherita Ligure, Italy*

3. Vijay Kumar, **Invited talk**, Magnetic properties of nanomaterials, in Workshop on Computational Nanoscience, Shiv Nadar University, April 04, 2014

4. Vijay Kumar, **Plenary talk**, Applications of DFT in Materials Science, Workshop on electronic structure, atomistic and statistical modeling in Chemistry, Materials and Life Sciences, October 8-10, 2014, Department of Chemistry, University of Delhi, Delhi Schrödinger Materials Science Suite

5. Vijay Kumar, **Invited talk**, *Magnetic superatoms and magnetism in nanoalloys,* DAE BRNS Symposium on Multiscale Modelling of Materials and Devices (MMMD - 2014) October 30 – November 02, 2014

6. Vijay Kumar, **Plenary talk**, Magnetism in Nanoalloys, SCIMEETING 2014, Dalian, September 11-13, 2014, Multiscale Modelling & Simulations for Product and Process Design

7. Vijay Kumar, **Invited talk**, Clusters as superatoms and assemblies to develop magnetic materials, IWCCMP-2014, ABV-IIITM, Gwalior, November 29 – 30, 2014

8. Vijay Kumar, **Invited talk**, Accelerating Innovations of Novel Materials using Computer Simulations, USPEX8 Workshop, Shiv Nadar Univ. Jan 20-24, 2015

9. Vijay Kumar, **Invited talk**, Computational Design of Nanomaterials, CTCMP-2015 NISER,India February 19 – 22, 2015

10. Vijay Kumar, **Invited talk**, Magnetism in nanoalloys and assemblies, Advances in Computational Materials Science CUTN, Thiruvarur, April 23-25, 2015

11. B.L. Chittari and **Vijay Kumar**, **Hot topic oral presentation** Nanoparticles by design: $Fe_{75}Pt_{72}$, in ISSPIC 17 Conference in Fukuoka, Japan, Sept. 7-12, 2014.

12. B.L. Chittari and **Vijay Kumar**, **Poster presentation**, Alternate shell structure in Fe-Co nanoparticles, in ISSPIC 17 Conference in Fukuoka, 7-12 Sept. 2014, Japan

13. B.L. Chittari and **Vijay Kumar**, **Poster presentation**, H and O adsorption on $Fe_{13}Pt_{42}$ core-shell nanoparticle, in ISSPIC 17 Conference in Fukuoka, Japan, 7-12 Sept. 2014.

14. **B. L. Chittari** and Vijay Kumar, **Poster presentation**, Atomic structure and magnetic behaviour of Fe-Pt clusters and nanoparticles, International Symposium on Multi-scale Modeling and Simulation of Materials. - Joint *ICTP*-NSFC School and Advanced Workshop, *Fudan* University, Shanghai, China, July 8-12, *2013*

15. **Bheema Lingam Chittari** and Vijay Kumar, **Oral presentation**, Designing rare-earth-free strong magnets from *ab initio* calculations, in ICCP9, NUS, Singapore, 7-11 Jan. 2015'

16. **Bheema Lingam Chittari** and Vijay Kumar, Poster presentation, Designing FePt-Fe_3Pt hard-soft magnetic composite materials from *ab initio* calculations, International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods, 15-17 Jan. 2015, ICTP, Trieste, Italy

d) manuscripts submitted but not yet published

1. B.L. Chittari and Vijay Kumar, Atomic structure, alloying behaviour, and magnetism in small Fe-Pt clusters, Phys. Rev. B almost accepted (minor comment)

2. B.L. Chittari and Vijay Kumar, Structural anisotropy and high energy product in FePt-Fe_3Pt hard-soft magnet nano-composites from *ab initio* calculations

3. Sandeep Kumar Jain, Bheema Lingam Chittari, and Vijay Kumar, Optimum thickness of hard/soft magnetic phases in FePt/FeCo permanent magnet superlattices with high energy product and large magnetic anisotropy energy, almost ready for submission

Note: A manuscript on FePt/Fe superlattices is under preparation. Work on CoPt/FeCo and FePt/Fe_3Pt superlattices to be written up. Also work on charged clusters is needed to be written up.

e) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

1. Vijay Kumar, **Invited talk***, Ab Initio* Design of Nanomaterials with Tunable Properties by Doping, US-India Technical Exchange Meeting on Tunable Materials, Tec Edge (Wright Brothers Institute), Dayton, 25 – 27 March 2014

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